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MECHANISMS OF FATIGUE DAMAGE AND FRACTURE IN SEMI-CRYSTALLINE P--ETC(U)

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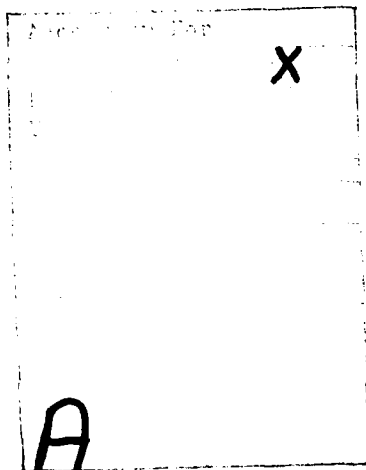
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MECHANISMS OF FATIGUE DAMAGE AND FRACTURE

IN SEMI-CRYSTALLINE POLYMERS

P. E. Bretz,¹ R. W. Hertzberg² and J. A. Manson²

Abstract

Fatigue crack profiles and fracture surfaces of poly(vinylidene fluoride) (PVDF), nylon 66 (N66), and poly acetal (PA) were studied to ascertain the mechanisms of cyclic damage and fatigue crack propagation in semi-crystalline polymers. Crack tip damage is believed to begin as small trans-spherulitic and interspherulitic tensile crazes. However, compressive yielding within the reverse plastic zone at the crack tip crushes and elongates the spherulites in the direction of crack growth. Consequently, the microstructure of the polymer in advance of the crack front is very different from the original morphology of the spherulitic bulk material as evidenced by the resulting fracture surface appearance. When the test temperature is below the glass transition temperature, however, plastic deformation is limited, and fatigue fracture occurs before significant disruption of the spherulitic structure. In this case, the fracture surface morphology reflects the original microstructure of the bulk polymer.

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Introduction

When a fatigue crack propagates through a solid, it may generate a fracture surface that reflects the underlying bulk microstructure. Consequently, the fracture surface appearance of a semi-crystalline polymer under certain test conditions may closely reflect the spherulite morphology of this material. Since the fatigue crack is preceded by a zone of intense plastic deformation, however, the spherulite structure may be significantly altered by cyclic damage occurring within this zone prior to fracture. As a result, the morphology of the damage zone through which fracture occurs may be quite different from the bulk spherulite structure. It is necessary, therefore, to consider the manner by which a spherulitic structure deforms.

The tensile deformation of polymer spherulites has received considerable attention including several reviews¹⁻⁵ as well as numerous experimental investigations⁶⁻¹². It is generally agreed that initial damage takes place by deformation of the spherulites, followed by the transformation of spherulites into fibrils which are themselves subsequently elongated. Several authors have noted that the earliest damage takes place by cavitation in interlamellar regions within the spherulites^{1,7-9,11}, primarily in the equatorial plane perpendicular to the stress axis. Other studies have observed interspherulitic cavitation in addition to trans-spherulitic void formation^{2-5,10,12}. The actual structure of these void regions is not clear, but numerous studies have reported crazes in semi-crystalline polymers^{5,7-10,12}. In light of the small deformations at which this cavitation occurs and the unlikelihood of actual fracture at such low strains, the interpretation of void regions as crazes seems justified.

Several studies have also examined fatigue-induced damage and fracture. Kausch⁴ observed density fluctuations in PA resulting from cyclic loading and interpreted these fluctuations as reflecting the presence of inter-lamellar microvoids perpendicular to the load axis. In this same study, Kausch proposed a model for subcritical crack growth in semi-crystalline polymers which assumed both inter and trans-spherulitic crazing ahead of the crack tip. Andrews and Walker¹³ observed trans-spherulitic fracture in low density polyethylene at low crack growth rates and secondary inter-spherulitic cavitation around the crack plane. It appears, therefore, that cyclic damage in semi-crystalline polymers is related to cavitation within and around the spherulites.

When comparing the consequences of tensile versus cyclic loadings, it is not clear whether the deformations that occur within the plastic zone at the crack tip during cyclic loading are comparable to deformations produced in a tensile test under monotonic loading conditions. Regarding the fatigue crack tip plastic zone, a zone of monotonic tensile plastic deformation can be identified ahead of the fatigue crack tip (Figure 1a). Within this zone, one finds a smaller volume of material which experiences compressive loads equal to the specimen yield strength (Figure 1b). This region of reverse plasticity is created when the applied load decreases to the minimum tensile value; to maintain a stress balance along the crack plane, the crack tip region must go into compression^{14,15}. Therefore, the material at the crack tip undergoes alternating tensile and compressive yielding. The effect of this load history on the spherulite morphology of a semi-crystalline polymer is unknown. For this reason, an examination of the crack tip region in several semi-crystalline polymers was undertaken to ascertain the effect of cyclic damage on the spherulite structure.

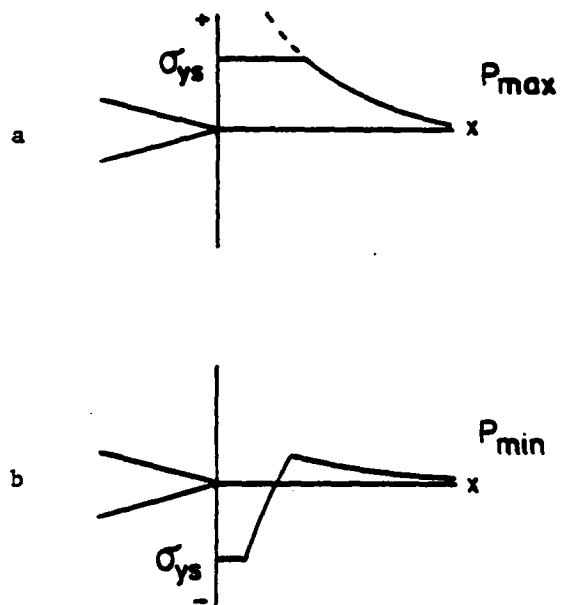


Figure 1 Crack tip stress distribution at
a) maximum load, b) minimum load.

Experimental Procedure

The specimens examined in this study had been previously used to characterize the fatigue crack propagation (FCP) behavior of several polymers, including nylon 66 (N66)¹⁶⁻¹⁹, poly(vinylidene fluoride) (PVDF)¹⁹, and poly acetal (PA)¹⁹⁻²⁰. In the case of N66, a series of specimens were equilibrated at various levels of absorbed moisture prior to fatigue testing¹⁶⁻¹⁹. All tests were conducted at room temperatures at a sinusoidal frequency of 10 Hz except for the PA material which was tested at 100 Hz.

The damage zone surrounding the fatigue crack was studied by sectioning test specimens at mid-thickness in a plane parallel to the specimen surface. The region of interest was mounted in 2.54-cm-diameter bakelite rings by casting an epoxy resin in the ring. Specimens were rough-ground through a series of wet papers, ending with 600 grit. Final polishing was accomplished using alumina powders in an aqueous slurry, starting with 1 μ m powder and ending with 0.3 μ m. A variety of etchants, both solvent and oxidizing, were used on the polymers with success and are listed below.

N66	2 parts glycerin 1 part HNO ₃ 2 parts H ₂ O etch at room temp. for 1 min.
PVDF	etch in acetone at room temp. for 30 min.
PA	7 parts HNO ₃ 13 parts H ₂ O etch for 15 min. at room temp.

The fatigue crack surfaces were studied using a Zeiss Axiomat optical microscope and an ETEC auto-scan scanning electron microscope (SEM). For the latter instrument, a 20-kV accelerating voltage was used for all investigations except those of PA, for which the voltage was limited to 5 kV to minimize beam damage to the fracture surface. Prior to SEM observation, specimens were prepared either by vacuum evaporation of gold and carbon or by sputter-coating from a gold-palladium target.

Experimental Results and Discussion

Metallographic Observations

During FCP testing of PVDF and N66 (water content > 0.8 wt%) a whitened region at the crack tip was observed. Since the occurrence of such stress-whitening signals a change in the structural morphology of the polymer, it was felt that this whitened region might be related to the plastic zone at the crack tip. In a subsequent experiment involving a specimen of PVDF, a fatigue crack was grown to a ΔK level of $5 \text{ MPa}\sqrt{\text{m}}$, at which point the test was stopped and the crack tip region removed from the test plaque for observation (Figure 2).^{*} The whitened zone clearly extends on either side of the actual crack, as well as several millimeters in front of the crack tip. It is interesting that the shape of this whitened zone is planar, reminiscent of the Dugdale model for crack tip plasticity²¹. Previously, this model was found useful in characterizing the extent of cyclic-induced damage in amorphous polymers^{22,23}. In this investigation, the extent of whitening in samples of PVDF was in reasonable agreement with the Dugdale zone length (5.1 mm) at this ΔK level, as calculated from the following equation²¹:

$$R = \frac{\pi}{8} \left(\frac{K}{\sigma_{ys}} \right)^2 \quad (1)$$

where R = zone length

K = maximum stress intensity factor

σ_{ys} = material yield strength

We conclude, therefore, that the whitened area delineates the plastic zone region at the advancing crack tip. Similar observations were made in moisture-

^{*} Crack propagation direction is from left to right in all photographs unless marked otherwise.

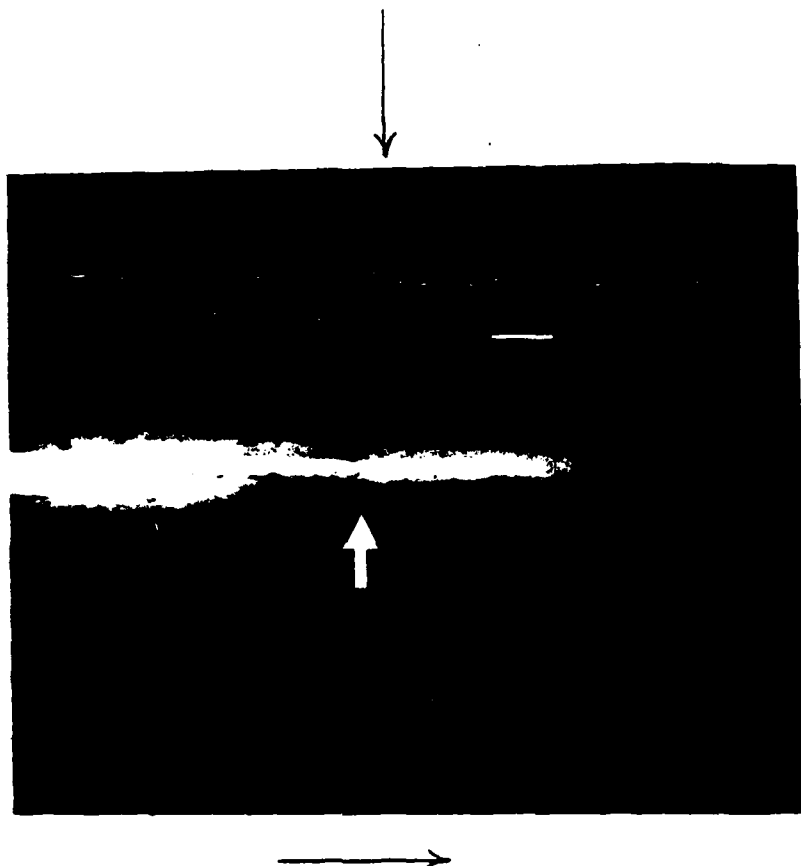


Figure 2 Crack tip profile in PVDF (vertical arrow denotes crack tip). Horizontal arrow indicates crack growth direction. Scale bar = 1 mm

containing polyamides. For example, Figure 3 shows the mid-thickness profile for half of a fully fractured specimen of N66 containing 2.2% water. Again, a whitened zone flanks the fracture plane, verifying that the crack propagated through a damage zone at the crack tip.

Returning to Figure 2, a smaller, more intense whitened zone was visible within the diffuse region of whitening. It was noticed that after metallographic polishing this smaller zone had collapsed below the polishing plane, leaving a long dimple on the surface with the dimensions of the intense whitened zone. Since the polishing plane was located at mid-thickness of the test specimen, the observed dimpling is believed to reflect a relaxation of the through-thickness stress (σ_z). Such sectioning and subsequent polishing of PVDF samples in aqueous slurries and etching in acetone was apparently sufficient to induce relaxation of this region, thereby causing the surface dimple.

On closer inspection, no distinct structure could be seen within the intense damage zone adjacent to the fracture surface. Within the more diffusely whitened region which surrounds the intense damage zone, thread-like markings (the dark wavy lines) were noticeable as shown in Figures 4 and 5 for the case of PVDF and N66. Note that the spherulitic microstructure remains visible (though damaged) in the diffuse whitened zone. We conclude that the diffuse whitened zone corresponds to the region where the spherulites are damaged though still basically intact. On the other hand, the intense whitened zone represents a region of severe damage, with the spherulitic structure having been broken down to an unrecognizable morphology.



Figure 3 Fracture profile for one-half of a fatigue specimen of N66 containing 2.2% H_2O . Note increasing depth of whitened region at high ΔK levels. Scale bar = 2mm

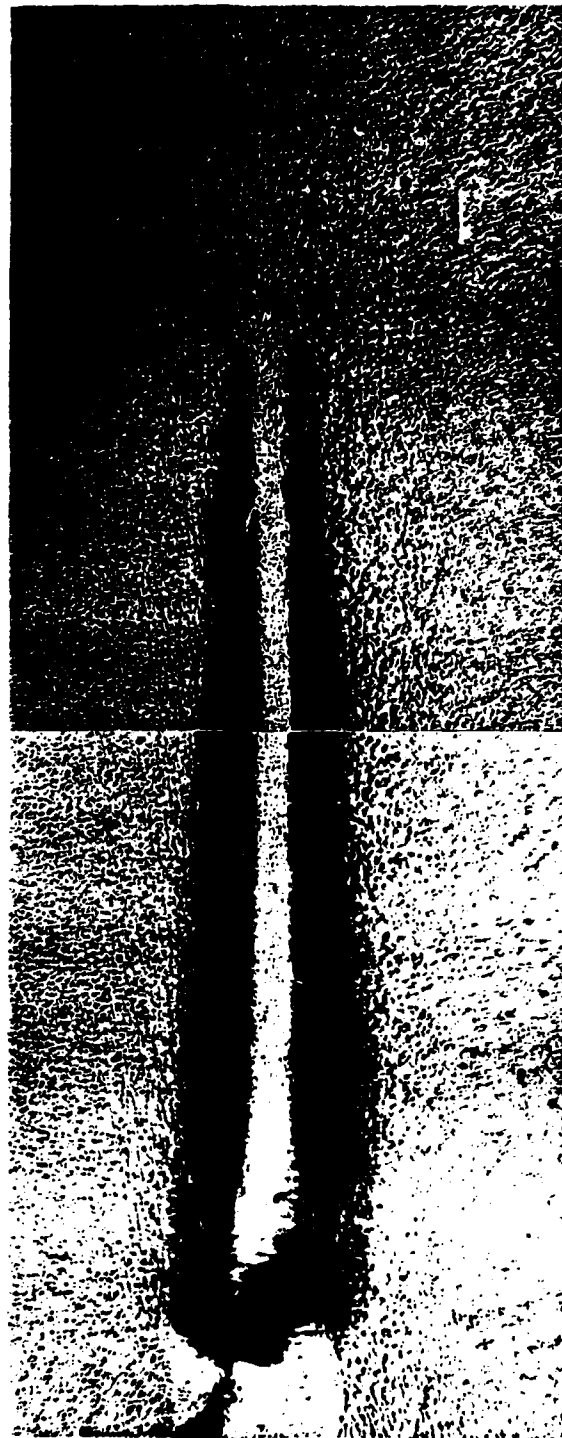
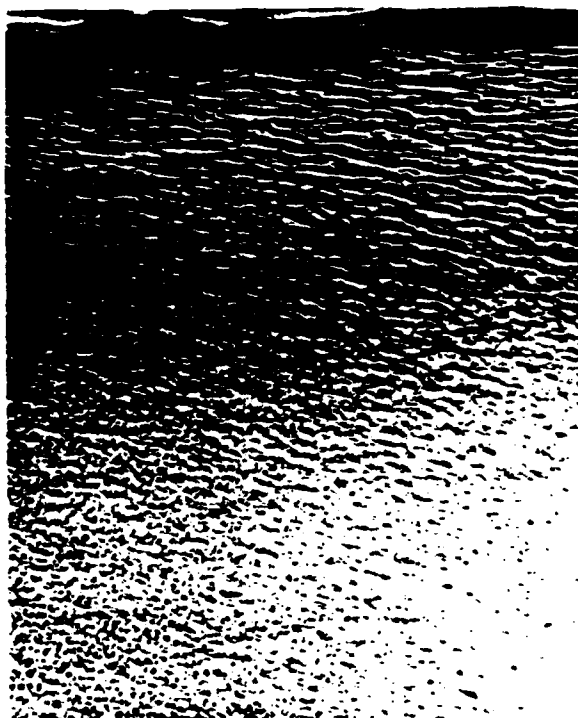


Figure 4 Region of intense whitening at crack tip in PVDF associated with lack of structural detail. Note thread-like features which flank this zone. Scale bar = 0.1 mm.

(a)



(b)

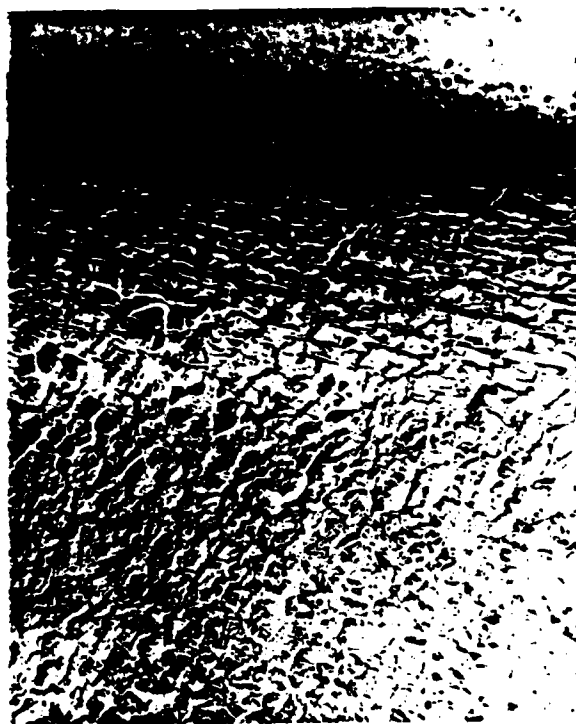


Figure 5 Thread-like markings flanking the fracture surface in a) PVDF (Scale bar = 0.5 mm), b) N66 (2.2% H₂O) (Scale bar = 40 μ m).

The nature and formation of these thread-like features deserves further comment. As mentioned above, the spherulite structure was undisturbed at large distances from the crack plane (i.e., outside the plastic zone). Somewhat closer to the crack plane, (i.e., in the diffuse whitened zone), small fissures parallel to the crack were visible (Figure 6a) and found to be both inter and trans-spherulitic in nature. In light of numerous reports of crazing in semi-crystalline polymers^{5,7-10,12}, it seems likely that these fissures are, indeed, crazes. The evidence for both inter and trans-spherulitic crazing is also supported by published results^{2-5,10,12}. Thus, it seems that cyclic loading initially induces local crazing in the weak interlamellar and interspherulitic regions.

Closer to the fracture surface, the crazes appeared to lengthen and coalesce (Figure 6b). It is interesting to note that the distance between these thread-like markings is roughly equal to the spherulite size in the polymer (15 μm in PVDF). The crazes seemed to propagate without significant disruption of the spherulites themselves, other than the bisection of spherulites by trans-spherulitic crazing. Such deformation is in agreement with the model proposed by Kausch⁴ and consistent with observations made of many semi-crystalline polymers¹⁻¹² under tensile loading. However, a simple tensile load does not create the reverse plastic zone at the crack tip which exists during FCP testing (see Figure 1b). This distinction is crucial, because the spherulites at the crack tip undergo compressive yielding during cyclic loading. Hence, the spherulites within the reverse plastic zone may be alternately crushed during compression but then subjected to high tensile stresses during the tensile portion of the loading cycle.

(a)



(b)

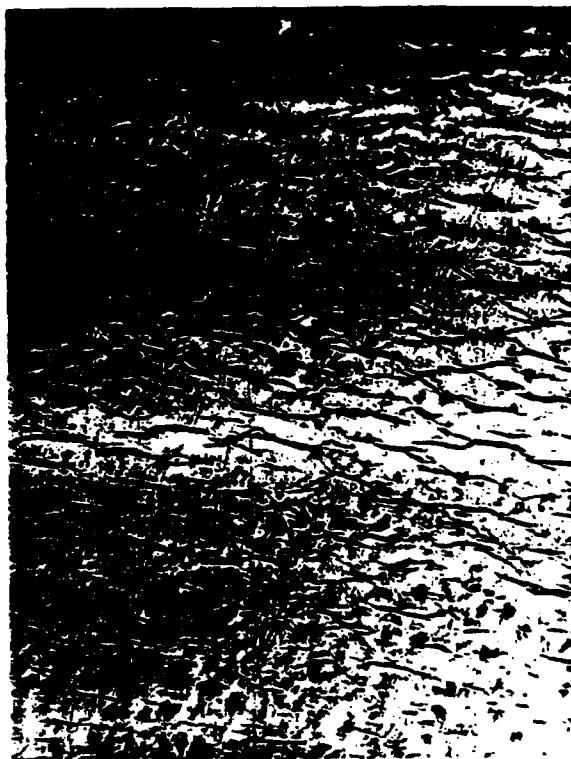


Figure 6 Trans-spherulitic and interspherulitic fissures in PVDF a) ~ 1 mm below fracture surface, b) immediately below fracture surface. Scale bar = 0.1 mm

Modification of the spherulite structure at the crack tip by this complex loading is believed to occur in the following manner. As described previously, initial cyclic damage occurs in tension by interspherulitic and trans-spherulitic craze formation. In this crazed spherulite structure, tensile strains are accommodated within the crazes themselves, leaving the spherulites undisturbed. However, compressive loads within the reversed plastic zone cannot be borne by the craze fibrils. Instead, they would be expected to collapse readily, thereby subjecting the spherulite to the crushing impact of the compressive portion of the loading cycle. As a result, the spherulites would be expected to flatten progressively in the crack propagation direction. Eventually remnants of the spherulites become so thin that the original structure no longer is discernible within the intense whitened zone (Figure 4). The compressive yielding and deformation of spherulites prior to fracture, therefore, has important implications with regard to the appearance of any remnants of the spherulite structure on the fracture surface itself, as will be discussed below. Finally, observation of the actual crack path (Figure 2) reveals that propagation does not occur through the middle of the reverse plastic zone. Rather, the fracture seems to jump randomly from the upper to lower interfaces between the reverse and monotonic plastic zones. The reason for this behavior is not clear.

The Model

The following deformation scenario is proposed for the cyclic loading of a semi-crystalline polymer containing a crack:

1. Fatigue damage begins as cyclic-induced crazing in interlamellar regions within spherulites and in interspherulitic regions. These crazes are on the order of the spherulite diameter in length, and the craze plane is perpendicular to the stress axis. Such damage occurs in the monotonic region of the plastic zone where only tensile stress and strains are encountered.

2. With increasing stresses and strains, the crazes begin to lengthen and eventually link together to form long, roughly parallel crazes which are much larger than the spherulite dimensions. The regions between the crazes consist of essentially undeformed spherulites, and tensile strains are accommodated within the crazes themselves.
3. Once inside the reverse plastic zone, the spherulite/craze structure is deformed by both tensile and compressive yielding. The spherulites are progressively crushed and smeared out, while tensile strains are still accommodated by the crazes. Eventually, the spherulite structure is completely destroyed by cyclic compression.
4. Finally, the fatigue crack passes through the heavily deformed region: apparently, though, the crack propagates near the lateral boundary between the reverse plastic zone and the monotonic plastic zone which contains the crazed spherulitic structure.

This deformation model is similar to those proposed by Andrews and Walker¹³ and by Kausch⁴. However, these authors did not consider the fact that, during cyclic loading, the crack tip region experiences compressive yielding prior to fracture. The damage which is presumed to occur within the reverse plastic zone is seen to degrade the original spherulite structure in a manner not previously envisioned nor foreseeable from a consideration of only tensile deformation of spherulites.

Fractographic Observation

At high ΔK levels ($> 4 \text{ MPa}\sqrt{\text{m}}$) in PVDF and moisture-bearing N66 ($> 0.8\% \text{ H}_2\text{O}$), the fracture surface was covered with long, ribbon-like features parallel to the crack growth direction (Figure 7). Interestingly,

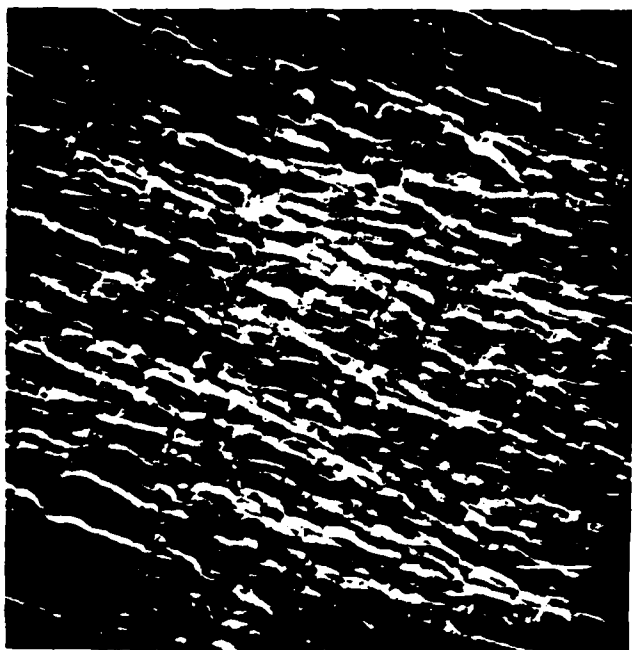


Figure 7a Ribbon-like features parallel to crack growth direction in N66 (2.2% H₂O). Arrows on micrograph indicate width of these ribbons, which are believed to be deformed spherulites.
 $\Delta K = 5.7 \text{ MPa}\sqrt{\text{m}}$ Scale bar = 50 μm

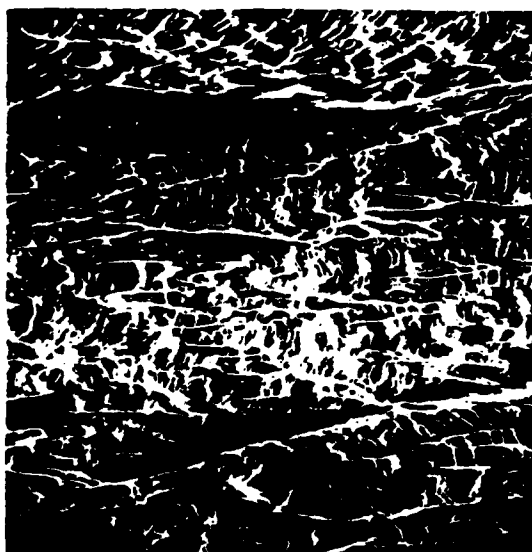


Figure 7b Deformed spherulites (width marked by arrows) in PVDF. Scale bar = 0.1 mm

the width of these ribbons at their widest points was close to the bulk spherulite size (15 μm in PVDF, 5-12 μm in N66). This correspondence in dimension compares with the observations of White and Teh^{24,25}, who found similar features in low density polyethylene; they concluded that these markings represented the original spherulites which had subsequently been drawn out in the direction of crack growth. The deformation model proposed in this paper predicts such spherulitic deformation by compression perpendicular to the crack plane and accounts for the elongation of the spherulites on the crack plane and in the crack growth direction. Under plane strain conditions, the through-thickness strain ϵ_z (which would tend to cause spherulite elongation perpendicular to the crack growth direction) is zero. While true plane strain conditions did not exist in these test specimens at higher ΔK levels, it is expected that deformation in the through-thickness direction was still restricted, such that compressive yielding of the spherulites would be expected to cause the spherulites to simply spread out parallel to the crack growth direction. It is concluded, therefore, that these fracture markings are indeed the remnants of spherulites which had been elongated by crack tip plastic deformation.

Additional Observations

It has been assumed in the previous discussions that the polymers under study possessed a sufficient capacity for plastic deformation within the spherulite structure so as to allow for gross changes in the spherulite morphology. In essence, this would imply that the polymer must be above or relatively near T_g , since it is unlikely that a semi-crystalline polymer with a T_g significantly above ambient test temperatures could accommodate such intense plastic deformation. Indeed, the glass temperature of PVDF is -35°C ²⁶, which is consistent with the discussion above. Similarly, T_g

for N66 decreases from 37°C at a moisture level of 2.2% (the lowest at which whitening and the microscopic evidence of crack tip deformation was seen) to -15°C at saturation²⁷. It is also worth noting that the fatigue damage in LDPE reported by White and Teh^{24,25} occurred in a polymer whose T_g is below -100°C²⁸.

It is interesting to speculate on the condition where T_g is significantly above the temperature of the FCP test. The fracture behavior of dry N66 [$T_g = 80^\circ\text{C}$ ²⁷] and PA [$T_g = 150^\circ\text{C}$ ²⁹] indicates that the spherulite structure is not perturbed to a noticeable depth below the crack plane (Figure 8). Although the actual fracture path is not clear in Figure 8a because of the small size of the spherulites in N66 (~5 μm in diameter), it is obvious that the crack in PA (Figure 8b) propagated in a trans-spherulitic manner. Moreover, the fracture surfaces of both dry N66 and PA showed definite evidence of trans-spherulitic fracture²⁰. This behavior represents a special case of the proposed deformation model in which the polymer structure is not able to support large plastic strains in the craze regions. In this instance, the short crazes presumably fracture prematurely, and the fatigue crack propagates by seeking out the local microcracks.

The assumption of cyclic-induced crazing in semi-crystalline polymers is seemingly at odds with the work of Bucknall and Stevens³⁰. In an examination of the shape of hysteresis loops for rubber-modified styrene blends, these authors concluded that crazing will cause asymmetry in the loop, since there is no analogue to tensile craze deformation during the compressive half of the bad cycle. In light of the fact that the hysteresis loop for nylon is symmetric³¹, one might conclude that crazing does not occur in nylon and the proposed deformation model is incorrect. This line of reasoning, however, ignores the considerable evidence for crazing in semi-

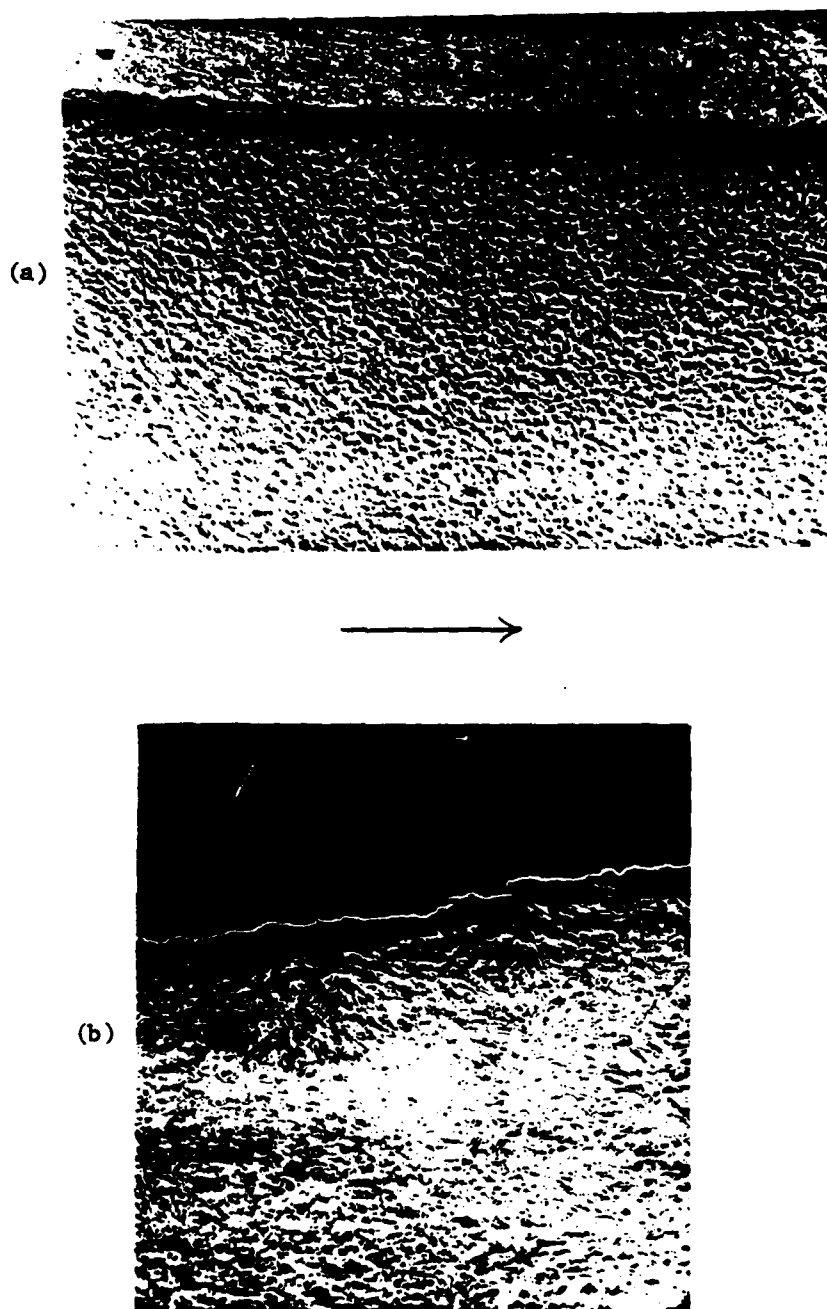


Figure 8 Fracture profiles in a) N66 containing 0% H_2O ,
b) PA (note evidence of trans-spherulitic fracture).
Scale bar = 50 μm

crystalline polymers including nylon. Also, Bucknall and Stevens concluded that fatigue damage in ABS does not occur predominantly by crazing, since the hysteresis loop for this blend is symmetric. However, the occurrence of discontinuous fatigue crack growth in ABS³² indicates that crazing does precede FCP in this blend. Similarly, polycarbonate exhibits a DG mechanism^{22,23} although the hysteresis loop for this polymer is symmetric³³.

Implicit in the above discussion was an assumption that stress-strain conditions in the unnotched and notched samples from the various investigations were directly comparable. Surely, this can not be the case; for example, the incidence of DGB formation itself varies with test conditions in a number of polymers. Therefore, inferences regarding the shape of the hysteresis loops from unnotched test samples can not, in themselves, provide definitive indications of the fatigue damage mechanisms in samples containing pre-existing flaws.

In closing, it should be noted that stress whitening during FCP tests does not automatically prove that significant plastic deformation has occurred at the crack tip. It is true that PVDF and the moisturized N66 samples which showed severe crack tip deformation exhibited stress-whitening; alternately, dry N66, which did not show any significant crack tip plasticity, did not stress-whiten. However, the fracture surfaces of all the PA specimens were stress-whitened noticeably despite the absence of any massive crack tip deformation. In this instance whitening most likely resulted from craze damage within and around the spherulites. Therefore, a determination of the extent of crack tip plasticity and the resultant processing of the semi-crystalline spherulite morphology must be made by microscopic examination of the fracture region, instead of relying on macroscopic fracture surface appearance alone.

Conclusions

A cyclic damage mechanism is proposed to explain the crack tip deformation patterns observed in semi-crystalline polymers capable of extensive plasticity. Fatigue damage is believed to occur initially by inter and trans-spherulitic crazing. However, the cyclic compression which occurs in the near crack-tip regions crushes the spherulites and elongates them in the direction of crack growth. As a result, the structure of the polymer within this plastic zone (through which crack propagation occurs) may be quite different from the bulk spherulite morphology. When material plasticity is limited, spherulite breakdown does not take place and the fracture surface morphology reflects the underlying microstructure.

Acknowledgements

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